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(54) NONAQUEOUS SECONDARY BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To enhance the energy quantity of a lithium secondary battery and also enhance the cycle life.

SOLUTION: In a nonaqueous secondary battery comprising a positive electrode having a positive electrode active material, a negative electrode having a negative electrode material, and a nonaqueous electrolyte as components, the positive electrode active material consists of a lithium-containing transition metal oxide, the negative electrode material consists of a silicon-containing compound capable of inserting and releasing lithium, and the current collector of the negative electrode consists of a metal support body which has an average roughness of 0.03 μm or more and 1 μm or less and a thickness of 5 μm or more and 100 μm or less.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the long lithium secondary battery of a cycle life by the nonaqueous rechargeable battery, especially high capacity.

[0002]

[Description of the Prior Art] The lithium contained in positive active material is first inserted in a negative-electrode ingredient, and the activity of a negative-electrode ingredient is raised in the lithium secondary battery using the positive active material containing the negative-electrode ingredient which does not contain a lithium metal, and a lithium. This is a charge reaction and the reaction for which a lithium ion is made to insert in positive active material from the reverse negative-electrode ingredient is a discharge reaction. Carbon is used as this type of a lithium cell negative-electrode ingredient. The geometric capacity of carbon (C6 Li) is 372mAh(s)/g, and further high capacity negative-electrode ingredient is desired. On the other hand, the geometric capacity of the silicon which forms a lithium and an intermetallic compound surpasses 4000mAh(s)/g, and it is known well that it is larger than that of carbon. For example, the silicon of a single crystal is indicated in JP,5-74463,A, and amorphous silicon is indicated in JP,7-29602,A. moreover, the example which contains silicon in a Li-aluminum alloy with the alloy containing silicon -- JP,63-66369,A (silicon is 19 % of the weight) -- said -- 63-174275 (silicon is 0.05 - 1.0 % of the weight) -- said -- it is indicated by 63-285865 (silicon is 1 - 5 % of the weight). However, since each of such alloy patent application made the lithium the subject, the compound which does not contain a lithium was used for positive active material. Moreover, in JP,4-109562,A, 0.05 - 1.0% of the weight of the alloy is indicated for silicon. In JP,62-226563,A, the approach of mixing a lithium, the metal in which an alloy is possible, and graphite powder is indicated. However, it has come to use by all being inferior in a cycle life. As a reason which is inferior in the cycle life of silicon, the volume expands by that the electronic conduction nature is low and lithium insertion, and it is guessed that pulverization of the particle is carried out. On the other hand, as a charge collector of a negative electrode, although the foil of aluminum or copper is usually used, it cannot be said by the cell using these ingredients that a cycle life is enough, either. It is guessed that the flow between a charge collector and an electrode binder layer becomes large one of the causes with an inadequate cycle life.

[0003]

[Problem(s) to be Solved by the Invention] The purpose of this invention is to raise the amount of energy of a lithium secondary battery, and raise a cycle life.

[0004]

[Means for Solving the Problem] In the nonaqueous rechargeable battery which uses as a component the positive electrode which has positive active material, the negative electrode which has a negative-electrode ingredient, and nonaqueous electrolyte, this positive active material is lithium content transition-metals oxide, and the technical problem of this invention is a compound with which this negative-electrode ingredient contains the silicon atom in which insertion emission of a lithium is possible, and was able to be solved with the nonaqueous rechargeable battery characterized by for the

charge collectors of this negative electrode to be 5 micrometers or more in thickness, and a metallic foil base material 100 micrometers or less in 0.03 micrometers or more of average surface roughness, and 1 micrometer or less.

[0005]

[Embodiment of the Invention] Although the mode of this invention is explained below, this invention is not limited to these.

(1) The nonaqueous rechargeable battery characterized by for this positive active material being lithium content transition-metals oxide, being the compound with which this negative-electrode ingredient contains the silicon atom in which insertion emission of a lithium is possible in the nonaqueous rechargeable battery which uses as a component the positive electrode which has positive active material, the negative electrode which has a negative-electrode ingredient, and nonaqueous electrolyte, and the charge collectors of this negative electrode being 5 micrometers or more in thickness, and a metallic foil base material 100 micrometers or less in 0.03 micrometers or more of average surface roughness, and 1 micrometer or less.

(2) The nonaqueous rechargeable battery whose charge collectors given in a term (1) are copper, nickel, titanium or those alloys, and stainless steel.

(3) The nonaqueous rechargeable battery a term (1) or whose charge collector given in (2) is 0.05 micrometers or more of average surface roughness, and a metallic foil 0.5 micrometers or less.

→ (4) Term (1) The average grain size of a silicon compound given in - (3) is a nonaqueous rechargeable battery which is 0.01-100 micrometers.

(5) Term (1) Nonaqueous rechargeable battery whose silicon compound given in - (3) is an alloy.

(6) The nonaqueous rechargeable battery whose at least one sort of metals other than silicon is alkaline earth metal, transition metals, and semimetal in an alloy given in a term (5).

(7) The nonaqueous rechargeable battery whose at least one sort of a term (5) or a metal given in (6) is germanium, Be, Ag, aluminum, Au, Cd, Ga, In, Sb, Sn, and Zn.

(8) Term (5) Nonaqueous rechargeable battery whose weight ratio of this metal to silicon given in - (7) is 5 - 90%.

(9) The nonaqueous rechargeable battery whose silicon compound given in a term (1) is the silicon which removed the metal from the metal silicide.

(10) The nonaqueous rechargeable battery whose metal silicide given in a term (9) is a lithium silicide.

(11) The nonaqueous rechargeable battery whose lithium content of a lithium silicide given in a term (10) is 100 - 420 atom % to silicon.

(12) The nonaqueous rechargeable battery whose silicon compound given in a term (1) is a silicon compound with which it has adhered with the lithium and the ceramic which does not react.

(13) a ceramic given in a term (12) -- aluminum $2O_3$, SiO_2 , TiO_2 , SiC , and $Si_3 N_4$ from -- nonaqueous rechargeable battery which are at least one sort of ceramics chosen.

(14) The nonaqueous rechargeable battery whose weight ratio of this ceramic to a term (12) or a silicon compound given in (13) is 2 - 50%.

(15) Term (12) The manufacture approach of a negative-electrode ingredient that the method of making this ceramic adhere to the silicon compound of a publication includes the process heated at 300-1300 degrees C in - (14).

(16) The nonaqueous rechargeable battery with which the silicon compound of a publication is covered at least with the metal by the term (1).

(17) The manufacture approach of a negative-electrode ingredient that the approaches which a term (16) is made to cover with the metal of a publication are a nonelectrolytic plating method, vacuum deposition, the sputtering method, and a chemical-vapor-deposition method.

(18) The nonaqueous rechargeable battery whose at least one sort of the metal with which a publication is covered by a term (16) or (17) is nickel, Cu, Ag, Co, Fe, Cr, W, Ti, Au, Pt, Pd, Sn, and Zn.

(19) Term (16) Nonaqueous rechargeable battery whose specific conductance of the silicon compound covered with the metal of a publication by - (18) is 10 or more times of the specific conductance of the silicon compound which is not covered.

- (20) The nonaqueous rechargeable battery with which the silicon compound of a publication is beforehand covered with thermoplastics by the term (1).
- (21) The nonaqueous rechargeable battery whose thermoplastics given in a term (20) is polyvinylidene fluoride and polytetrafluoroethylene.
- [0006] (22) The nonaqueous rechargeable battery whose weight ratio of thermoplastics to a term (20) or a silicon compound given in (21) is 2 - 30%.
- (23) Term (20) Nonaqueous rechargeable battery whose coverage of thermoplastics given in - (22) is 5 - 100%.
- (24) The nonaqueous rechargeable battery using the negative electrode which made carbon live together 5 to 1900% by the weight ratio to the silicon compound of a publication in a term (1).
- (25) The nonaqueous rechargeable battery whose carbon given in a term (24) is a scale-like natural graphite.
- (26) The nonaqueous rechargeable battery whose x is within the limits of 0 to 4.2 as equivalent ratio of the lithium in which the charge-and-discharge range of a silicon compound given in a term (1) carries out insertion emission at silicon when expressed with Li_xSi .
- (27) The charge-and-discharge range of a silicon compound given in a term (1) is a nonaqueous rechargeable battery whose x is within the limits of 0 to 3.7 when expressed with Li_xSi .
- (28) Positive active material given in a term (1) is a nonaqueous rechargeable battery using at least one sort of the ingredient containing Li_yMO_2 ($\text{M}=\text{Co}$, nickel and Fe, $\text{Mn } y=0-1.2$), or the ingredient which has the Spinel structure expressed with $\text{Li}_z\text{N}_2\text{O}_4$ ($\text{N}=\text{Mn } z=0-2$).
- (29) Term (3) Nonaqueous rechargeable battery whose average grain size of silicon given in - (27) is 0.01-50 micrometers. The silicon said here is a lithium, the silicon simple substance which can react, a silicon alloy, and a silicide.
- (30) Term (5) Nonaqueous rechargeable battery which is the alloy with which the alloy of a publication adhered the ceramic of a publication to - (8) at term (9) - (15).
- (31) Term (5) Nonaqueous rechargeable battery which is the alloy with which the alloy of a publication covered the metal of a publication to - (8) at term (16) - (19).
- (32) The nonaqueous rechargeable battery which is the alloy with which the ingredient of a publication covered the metal of a publication in the term (30) at term (16) - (19).
- (33) Term (5) Nonaqueous rechargeable battery which is the alloy with which the alloy of a publication covered the thermoplastics of a publication to - (8) at term (20) - (23).
- (34) Term (30) Nonaqueous rechargeable battery which is the ingredient with which the ingredient of a publication covered the thermoplastics of a publication to - (32) at term (20) - (23).
- (35) Term (5) Nonaqueous rechargeable battery which made a term (24) or the carbon of (25) live together into an alloy given in - (8).
- (36) Term (30) Nonaqueous rechargeable battery which made a term (24) or the carbon of (25) live together into an ingredient given in - (34).
- (37) Term (5) Nonaqueous rechargeable battery which used the alloy of a publication for - (8) a term (26) or in [charge-and-discharge] (27).
- (38) Term (30) Nonaqueous rechargeable battery which used the ingredient of a publication for - (34) a term (26) or in [charge-and-discharge] (27).
- (39) Term (5) Nonaqueous rechargeable battery using the compound of a term (28) as positive active material of an alloy negative electrode given in - (8).
- (40) Term (30) Nonaqueous rechargeable battery using the compound of a term (28) as positive active material of an ingredient given in - (36).
- (41) Term (9) Nonaqueous rechargeable battery which is the silicon with which the silicon of a publication made the ceramic of a publication adhere to - (11) at term (12) - (15).
- (42) Term (9) Nonaqueous rechargeable battery which is the silicon with which the silicon of a publication covered the metal of a publication to - (11) at term (16) - (19).
- (43) The nonaqueous rechargeable battery which is the ingredient with which the ingredient of a publication covered the metal of a publication in the term (41) at term (16) - (19).

- (44) Term (9) Nonaqueous rechargeable battery which is the silicon with which the silicon of a publication covered the thermoplastics of a publication to - (11) at term (20) - (23).
- (45) Term (41) Nonaqueous rechargeable battery which is the ingredient with which the ingredient of - (43) covered the thermoplastics of a publication to term (20) - (23).
- (46) Term (9) Nonaqueous rechargeable battery whose silicon given in - (11) is silicon which made a term (24) or the carbon of (25) live together.
- (47) Term (41) Nonaqueous rechargeable battery whose ingredient given in - (45) is an ingredient which made a term (24) or the carbon of (25) live together.
- (48) Term (9) Nonaqueous rechargeable battery which used the silicon of a publication for - (11) in a term (26) or the charge-and-discharge range given in (27).
- (49) Term (41) Nonaqueous rechargeable battery which used the ingredient of a publication for - (47) in a term (26) or the charge-and-discharge range given in (27).
- (50) Term (9) Nonaqueous rechargeable battery using the compound of a term (28) as positive active material of a silicon negative electrode given in - (11).
- (51) Term (41) Nonaqueous rechargeable battery using the compound of a term (28) as positive active material of a negative electrode given in - (47).
- (52) Term (12) Nonaqueous rechargeable battery which is the silicon compound with which the silicon compound of a publication covered the metal of a publication to - (15) at term (16) - (19).
- (53) Term (12) Nonaqueous rechargeable battery which is the silicon compound with which the silicon compound of a publication covered the thermoplastics of a publication to - (15) at term (20) - (23).
- (54) The nonaqueous rechargeable battery which is the ingredient with which the ingredient of a publication covered the thermoplastics of a publication in the term (52) at term (20) - (23).
- (55) Term (12) Nonaqueous rechargeable battery which made a term (24) or the carbon of (25) live together to a silicon compound given in - (15).
- (56) Term (52) Nonaqueous rechargeable battery which made a term (24) or the carbon of (25) live together into an ingredient given in - (54).
- (57) Term (12) Nonaqueous rechargeable battery which used the silicon compound of a publication for - (15) in a term (26) or the charge-and-discharge range given in (27).
- (58) Term (52) Nonaqueous rechargeable battery which used the ingredient of a publication for - (54) in a term (26) or the charge-and-discharge range given in (27).
- (59) Term (12) Nonaqueous rechargeable battery using the compound of a term (28) as positive active material of a silicon compound negative electrode given in - (15).
- (60) Term (52) Nonaqueous rechargeable battery using the compound of a term (28) as positive active material of an ingredient negative electrode given in - (54).
- (61) Term (16) Nonaqueous rechargeable battery whose ingredient given in - (19) is an ingredient to which the ceramic of term (9) - (15) was made to adhere.
- (62) Term (16) Nonaqueous rechargeable battery which is the ingredient with which the ingredient of - (19) covered the thermoplastics of a publication to term (20) - (23).
- (63) The nonaqueous rechargeable battery which is the ingredient with which the ingredient of a publication covered the thermoplastics of a publication in the term (61) at term (20) - (23).
- (64) The nonaqueous rechargeable battery which made a term (24) or the carbon of (25) live together into an ingredient given in term (16) - (19) and (61) - (63).
- (65) The nonaqueous rechargeable battery which used the ingredient of a publication for term (16) - (19) and (61) - (63) a term (26) or in [charge-and-discharge] (27).
- (66) The nonaqueous rechargeable battery using the compound of a term (28) as positive active material of an ingredient negative electrode given in term (16) - (19) and (61) - (63).
- (67) Term (20) Nonaqueous rechargeable battery which is the ingredient with which the ingredient of a publication adhered the ceramic of a publication to - (23) at term (9) - (15).
- (68) Term (20) Nonaqueous rechargeable battery with which the ingredient of a publication covered the metal of a publication to - (23) and (67) at term (16) - (19).
- (69) Term (20) Nonaqueous rechargeable battery whose ingredient given in - (23), (67), and (68) is an

ingredient which made a term (24) or carbon given in (25) live together.

(70) Term (20) Nonaqueous rechargeable battery which used the ingredient of a publication for - (23), (68), and (69) in a term (26) or the charge-and-discharge range given in (27).

(71) Term (20) Nonaqueous rechargeable battery using the compound of a term (28) as positive active material of an ingredient negative electrode given in - (23), (68), and (69).

(72) A term (24) or the nonaqueous rechargeable battery using a compound given [as positive active material of a negative electrode given in (25)] in a term (28).

[0007] the positive electrode (or negative electrode) used by this invention -- a positive electrode -- on a charge collector, a mixture (or a negative electrode mixture) can be painted and fabricated, and can be made. a positive electrode -- an others and electric conduction agent, a binder, a dispersant, a filler, an ion electric conduction agent, a pressure enhancement agent, and various additives can be included in a mixture (or a negative electrode mixture). [positive active material / (or negative-electrode ingredient)] Although these electrodes may be discoid and tabular, it is desirable to have the shape of a supple sheet.

[0008] The configuration and ingredient of this invention are explained in full detail below. As the quality of the material of the charge collector with which the negative electrode of this invention is used, they are copper, nickel, titanium simple substances, these alloys, or stainless steel. Copper or its alloy is mentioned as one of the quality of the materials of the desirable negative-electrode charge collector used by this invention. Although there are Zn, nickel, Sn, aluminum, etc. as copper and a desirable metal to alloy, small quantity, in addition ** are good for others in Fe, P, Pb, Mn, Ti, Cr, Si, As, etc. Titanium or its alloy is mentioned as one more of the quality of the materials of the desirable negative-electrode charge collector used by this invention. Since the oxide film is stable, to an oxidizing quality environment, titanium is completely corrosion resistance and can prevent the dissolution at the time of the deep discharge in this embodiment, or overdischarge. Moreover, in order to improve corrosion resistance further, an alloy with Ta, Pd, Mo, nickel, or Zr may be used. As a metal to alloy, there are aluminum, Cr, Sn, Fe, Si, Mn, Cu, V, other Bi, etc. Nickel or its alloy is mentioned as another quality of the material of the desirable negative-electrode charge collector used by this invention. The oxide skin of nickel is precise, its protective action is large, and since it is excellent also in conductivity, it is desirable as a charge collector of this invention negative-electrode active material. The alloy which makes nickel a subject can also be used, for example, an alloy with Cu, Cr, Fe, Mo, Si, W, or Ta is desirable. Otherwise, an alloy with aluminum, Nb, Mn, Co, etc. is sufficient.

[0009] Stainless steel is mentioned as another quality of the material of the desirable negative-electrode charge collector used by this invention. Stainless steel is Fe-Cr steel excellent in weatherability and corrosion resistance which contains chromium about 11% or more. This alloy generates a passive state coat very thin on that front face in atmospheric air, and subsequent corrosion is hardly produced. Stainless steel is classified into a martensite system, a ferrite system, austenite, ferrite austenite, and semi-austenite by the metal texture. Austenitic stainless steel belongs to a Fe-Cr-nickel system or a Fe-Cr-Mn system, and shows an austenite texture, and it has high reinforcement and the outstanding ductility in the large temperature requirement ranging from the low temperature to an elevated temperature. It becomes a nonmagnetic perfect austenite texture by the solution treatment which quenches from the temperature of about 1000 Centigrade or more, and the outstanding corrosion resistance and the maximum ductility are acquired. As a desirable presentation of the stainless steel used by this invention, SUS304 and SUS316 of JIS, SUS316L, SUS430, etc. are mentioned, for example. It is the austenitic stainless steel which contains desirable SUS316 and Mo like SUS316L especially. The content of molybdenum is 1.7 to 4 % of the weight 6% of the weight in 1.2 7% of the weight from 1 preferably. The content of nickel is 10 to 15 % of the weight 16% of the weight in 9 18% of the weight from 8 preferably. The content of chromium is 16 to 19 % of the weight 20% of the weight in 15 26% of the weight from 11 preferably. When the combination of the content of nickel, chromium, and molybdenum is described in this order, they are 10 to 15 % of the weight, 16 to 19 % of the weight, and 1.7 to 4 % of the weight 6% of the weight in 1.2 7% of the weight from 1 preferably 9 to 16 % of the weight, and 15 to 20% of the weight 8 to 18 % of the weight, and 11 to 26% of the weight.

[0010] With the charge collector stated by this invention, it can use also as the base material of an

electrode, and a lead terminal. As a configuration of the charge collector in the case of using as a base material of an electrode, the shape of the shape of the shape of a foil and an expanded metal and a punching metal, the shape of a foaming metal, and a network is desirable, and is a foil-like most preferably. In order that the thickness of the charge collector used for this invention may raise the fill of an active material, the thinner one is good and 5micro-100micro are specifically 10micro-50micro desirable still more preferably. When the charge collector used for this invention is a continuum like a foil, a front face is processed physically or chemically, surface roughness may be changed or the thickness of an oxide skin may be adjusted, and a conductive paint film may be given or you may coat with silver, gold, TiC, TiN, etc.

[0011] As processing of surface roughening, although approaches, such as etching processings (acid treatment etc.), lasing, electrolytic plating, electroless deposition, and sandblasting, are in a metallic foil, it is not limited to these. Since it will cause cutting of a metallic foil etc. in process [coating, a press, etc.] in the viewpoint of compatibility with an active material content layer if it is too coarse although the coarser one of surface granularity is good, it is not desirable. As average surface roughness, the range of 0.03 micrometers or more and 1 micrometer or less is desirable. It is the range of 0.05 micrometers or more and 0.5 micrometers or less more preferably.

[0012] A charge collector may form a metal layer on both sides of a sheet plastic in order to make thickness thin. The thing of plastics excellent in ductility and thermal resistance is desirable, for example, it is polyethylene terephthalate. Only with a metal, since there is almost no elasticity, it is weak to external force. If a metal layer is formed on plastics, it will become strong against an impact. More specifically, a charge collector is a compound charge collector which covered base materials, such as a synthetic-resin film and paper, with the above-mentioned metal or alloy of electronic conduction nature. As a synthetic-resin film used as a base material, a fluororesin, polyethylene terephthalate, a polycarbonate, a polyvinyl chloride, polystyrene, polyethylene, polypropylene, polyimide, a polyamide, a cellulose dielectric, and polysulfone can be mentioned. As matter of the electronic conduction nature which covers a base material, it is desirable to use the above-mentioned copper, nickel, titanium simple substances, these alloys, or stainless steel. These compound charge collectors may be gestalten which make the sheet and metal sheet of a base material rival, and may form a metal layer by vacuum evaporation etc.

[0013] The compound containing the silicon atom which can carry out insertion emission of the lithium used with the negative-electrode ingredient of this invention means a silicon simple substance, a silicon alloy, and a silicide. A single crystal, polycrystal, and amorphous all can be used as a silicon simple substance. The purity of a simple substance has 85 desirable % of the weight or more, and its 95 % of the weight or more is especially desirable. Furthermore, especially 99 % of the weight or more is desirable. The average grain size has desirable 0.01-100 micrometers. Further 0.05-50 micrometers is more desirable, and especially 0.1-5 micrometers are desirable.

[0014] Since a silicon alloy controls the pulverization by expansion contraction of the silicon produced when insertion emission of the lithium is carried out or improves the conductive lowness of silicon, it is thought that it is effective. As an alloy, an alloy with alkaline earth metal, transition metals, or semimetal is desirable. Especially, a dissolution nature alloy and an eutectic nature alloy are desirable. A dissolution nature alloy says the alloy which forms the solid solution. For example, the alloy of germanium is a dissolution nature alloy. Although eutectic of the eutectic nature alloy is carried out to silicon at any rate, the solid-state cooled and obtained says the alloy which is the mixture of silicon and a metal. Be, Ag, aluminum, Au, Cd, Ga, In, Sb, Sn, and Zn form an eutectic nature alloy. In these, the alloy of germanium, Be, Ag, aluminum, Au, Cd, Ga, In, Sb, Sn, and Zn is still more desirable. Moreover, two or more sorts of these alloys are also desirable. The alloy which contains germanium, Ag, aluminum, Cd, In, Sb, Sn, and Zn especially is desirable. The mixed ratio of these alloys has 5 - 70 desirable % of the weight to silicon. Especially, 10 - 60 % of the weight is desirable. In this case, although electrical conductivity improves, it is desirable the cell engine performance and that specific conductance becomes 10 or more times of the specific conductance of the silicon in front of an alloy or a silicon compound in respect of discharge capacity, a high rate property, and a cycle life especially. The

average grain size of an alloy has desirable 0.01-40 micrometers. Especially, 0.03-5 micrometers is desirable.

[0015] A silicide says the compound of silicon and a metal. As a silicide, CaSi, CaSi₂, Mg₂ Si, and BaSi₂, SrSi₂, Cu₅ Si, FeSi, FeSi₂, and CoSi₂, nickel₂ Si, NiSi₂, MnSi, MnSi₂, and MoSi₂, CrSi₂, TiSi₂, Ti₅ Si₃, Cr₃ Si, and NbSi₂, NdSi₂, CeSi₂, SmSi₂, DySi₂, and ZrSi₂, WSi₂, W₅ Si₃, TaSi₂, Ta₅ Si₃, and TmSi₂, TbSi₂, YbSi₂, YSi₂, YSi₂, ErSi, ErSi₂, GdSi₂, PtSi, V₃ Si, VSi₂, HfSi₂, PdSi, PrSi₂, HoSi₂, EuSi₂, LaSi, RuSi, ReSi, RhSi, etc. are used.

[0016] As this silicon compound, the silicon which removed the metal from the metal silicide can be used. As a configuration of this silicon, a thing porous by the particle 1 micrometer or less and the thing which the minute particle condensed and formed the porous aggregated particle can be raised. It is thought as a reason a cycle life will be improved if this silicon is used that pulverization is hard to be carried out. As for the metal of this metal silicide, it is desirable that they are alkali metal and alkaline earth metal. Especially, it is desirable that they are Li, calcium, and Mg. Especially, Li is desirable. 100-420-mol% of the lithium content of this lithium silicide is desirable to silicon. Especially, 200-420 are desirable. As for the approach of removing alkali metal and alkaline earth metal from the silicide of alkali metal or alkaline earth metal, it is desirable to make it process with the solvent in which you react to with alkali metal and alkaline earth metal, and a resultant makes it dissolve. As a solvent, water and alcohols are desirable. The alcohols deaerated and dehydrated especially are desirable. As alcohols, methyl alcohol, ethyl alcohol, 1-propyl alcohol, 2-propyl alcohol, 1-butyl alcohol, sec-butylalcohol, t-butyl alcohol, 1-pentyl alcohol, 2-pentyl alcohol, and 3-pentyl alcohol are desirable. Especially, 1-propyl alcohol, 2-propyl alcohol, 1-butyl alcohol, sec-butylalcohol, and t-butyl alcohol are desirable. Removal of calcium or Mg has desirable water. It is still more desirable when a buffer for pH which is maintained near neutrality is used.

[0017] It is thought that the ceramic made to adhere to a silicon compound is effective in control of the pulverization of silicon. As a ceramic, a lithium and the compound which does not react in principle are desirable. Especially, they are aluminum 2O₃, SiO₂, TiO₂, SiC, and Si₃ N₄. It is desirable. As an approach to which silicon and a ceramic are made to adhere, although mixing, heating, vacuum evaporation, and CVD are used, concomitant use of mixing and heating is desirable especially. Especially, it is aluminum 2O₃. SiO₂ After carrying out distributed mixing of a sol and the silicon, it heats and the lump which dissolved is ground, and they are silicon and aluminum 2O₃. SiO₂ An affix can be obtained. in this case, aluminum 2O₃ SiO₂ an affix -- aluminum 2O₃ SiO₂ etc. -- that the front face is covered with silicon powder **** -- aluminum 2O₃ SiO₂ etc. -- the condition that it is shut up in the interior of a lump, or they are covered for the front face of silicon is said. Mechanical agitation, a supersonic wave, and kneading can attain mixed distribution. Although it is desirable to perform heating in 300 degrees C - 1300 degrees C in inert gas, 500 degrees C - 1200 degrees C are especially desirable. As for inert gas, an argon and nitrogen are raised. These mixed gas is also used. The approach by which the grinding method was learned with the ball mill, the vibration mill, the planet ball mill, the sufficient jet mill, etc. is used. It is desirable that this grinding is also performed in inert gas. Although the mixing ratio of the ceramics to silicon has 2 - 50% of the weight of the desirable range, 3 - 40% is especially desirable. The average grain size for which it asked from electron microscope observation of silicon has desirable 0.01-40 micrometers. Especially, 0.03-5 micrometers is desirable.

[0018] As metallic coating of the silicon compound of this invention, it can attain by vacuum deposition, such as electroplating, the permutation galvanizing method, a nonelectrolytic plating method, resistance heating vacuum deposition, electron beam evaporation, and cluster ion vacuum deposition, the sputtering method, and the chemical-vapor-deposition method (CVD method). Especially, vacuum deposition, such as a nonelectrolytic plating method, resistance heating vacuum deposition, electron beam evaporation, and cluster ion vacuum deposition, the sputtering method, and a CVD method are desirable. Furthermore, especially a nonelectrolytic plating method is desirable. A nonelectrolytic plating method is a volume on "nonelectrolytic plating foundation and application" electroplating study group. It is indicated by ***** (1994). The reducing agent has phosphinate, phosphonate, a boron hydride ghost, aldehydes, a saccharide, amines, and a desirable metal salt. Phosphinic acid

hydrogen sodium, phosphonic acid hydrogen sodium, a sodium borohydride, dimethylamine borane, formaldehyde, sucrose, a dextrin, a hydroxylamine, a hydrazine, an ascorbic acid, and a titanium chloride are desirable. It is desirable to include the pH regulator and complexing agent other than a reducing agent in plating liquid. The compound indicated above "a nonelectrolytic plating foundation and application" also about these is used. Although especially pH of plating liquid is not limited, 4-13 are desirable. For the temperature of liquid, although 10 degrees C - 100 degrees C are desirable, 20 degrees C - 95 degrees C are this better ** especially. It is SnCl₂ besides a plating bath. The activation bath which consists of a hydrochloric-acid water solution, and PdCl₂ The nucleation bath which consists of a hydrochloric-acid water solution is used, or a filtration process, a rinsing process, a grinding process, and a desiccation process are used further.

[0019] moreover -- as the gestalt of the silicon compound covered -- both the shape of fine particles massive tabular, etc. -- although -- it is used. Although the metal covered is good anything if it is a conductive high metal, nickel, Cu, Ag, Co, Fe, Cr, W, Ti, Au, Pt, Pd, Sn, and Zn are desirable especially. nickel, Cu, Ag, Co, Fe, Cr, Au, Pt, Pd, Sn, and Zn are desirable especially, and nickel, Cu, Ag, Pd, Sn, and especially Zn are still more desirable. Although especially the amount of metals covered does not have limitation, it is desirable to cover so that specific conductance may become 10 or more times of the specific conductance of the silicon compound which is a base.

[0020] It is desirable to cover with thermoplastics the silicon compound used by this invention. As for thermoplastics, a fluorine-containing high molecular compound, an imide system giant molecule, a vinyl system giant molecule, an acrylate system giant molecule, an ester system giant molecule, a polyacrylonitrile, etc. are used. Especially thermoplastics has desirable resin which is hard to swell in the electrolytic solution. As an example, polyacrylic acid, polyacrylic acid Na, a polyvinyl phenol, Polyvinyl methyl ether, polyvinyl alcohol, a polyvinyl pyrrolidone, Water-soluble polymers, such as polyacrylamide, PORIHIDOROKISHI (meta) acrylate, and a styrene-maleic-acid copolymer, Polyvinyl chloride, poly tetrapod FURURO ethylene, polyvinylidene fluoride, A tetra-FURURO ethylene-hexa FURURO propylene copolymer, a vinylidene fluoride-tetra-FURURO ethylene-hexa FURURO propylene copolymer, Polyethylene, polypropylene, an ethylene-propylene-diene terpolymer (EPDM), Sulfonation EPDM, polyvinyl-acetal resin, a methylmetaacrylate, The acrylic ester (meta) copolymer containing acrylic ester (meta), such as 2-ethylhexyl acrylate, The polyvinyl ester copolymer containing vinyl ester, such as an acrylic ester-acrylonitrile copolymer and vinyl acetate, (Meta) A styrene-butadiene copolymer, an acrylonitrile-butadiene copolymer, Polybutadiene, neoprene rubber, a fluororubber, polyethylene oxide, An emulsion (latex) or suspension, such as polyester polyurethane resin, polyether polyurethane resin, polycarbonate polyurethane resin, polyester resin, phenol resin, and an epoxy resin, can be mentioned. The latex of a polyacrylic ester system, a carboxymethyl cellulose, polytetrafluoroethylene, and polyvinylidene fluoride are mentioned especially. these compounds are independent -- or it can mix and use. Especially, a fluorine-containing high molecular compound is desirable. Polytetrafluoroethylene and polyvinylidene fluoride are desirable especially. As an approach of covering beforehand, thermoplastics is dissolved in a solvent, and a silicon compound is mixed and kneaded in the solution. The approach of drying the solution and grinding the obtained solid is desirable. As amount of the thermoplastics used to a silicon compound, 2 - 30 % of the weight is desirable. Especially, 3 - 20 % of the weight is desirable. Although 5 - 100% of coverage is desirable, 5 - 90% is desirable especially. The average size of the covered particle has 0.01 micrometers - desirable 40 micrometers. Especially, 0.03-5 micrometers is desirable.

[0021] It is desirable to mix and use a silicon compound and a carbonaceous compound in this invention. The ingredient for which a carbonaceous ingredient is used with an electric conduction agent or a negative-electrode ingredient is used. As a carbonaceous ingredient, a difficulty graphitized-carbon ingredient and a graphite system carbon material can be mentioned. Specifically JP,62-122066,A, JP,2-66856,A, The spacing indicated by each official report, such as 3-245473, a consistency, the carbon material of the magnitude of microcrystal, The mixture of a natural graphite and an artificial graphite given in JP,5-290844,A, JP,63-24555,A, 63-13282, 63-58763, They are a vapor growth carbon material given in JP,6-212617,A, and the ingredient by which heating baking was carried out at the temperature

exceeding 2400 degrees C in difficulty graphitized carbon given in JP,5-182664,A. And an ingredient with the peak of the X diffraction equivalent to two or more 002nd plane, JP,5-307957,A, 5-307958, 7-85862, the meso face carbon material compounded by the 8-315820 official report by pitch baking of a publication, To the graphite and pan which have the enveloping layer of a publication in JP,6-84516,A Carbon materials, such as the poly acene ingredient containing the baking object of various kinds of granules, a microsphere, a plate-like object, microfilament, the carbon material of the configuration of a whisker, phenol resin, acrylonitrile resin, and furfuryl alcohol resin and a hydrogen atom, etc. can be mentioned. Furthermore, as an example as an electric conduction agent, carbon materials, such as carbon black, such as graphite, such as artificial graphites, such as elevated-temperature baking objects, such as natural graphites, such as flaky graphite, a scale-like graphite, and an earthy graphite, petroleum coke, coal corks, celluloses, a saccharide, and a mesophase pitch, and a vapor growth graphite, acetylene black, furnace black, KETCHIEN black, channel black, lamp black, and thermal black, an asphalt pitch, a coal tar, activated carbon, a meso fuze pitch, and the poly acene, are desirable. These may be used independently and may be used as mixture.

[0022] Especially, the baking object of a carbon material given in JP,5-182664,A, various kinds of granules, a microsphere, a plate-like object, fiber, the carbon material of the configuration of a whisker and a mesophase pitch, phenol resin, and acrylonitrile resin and the poly acene ingredient which contains a hydrogen atom further are desirable. inside -- a scale-like natural graphite -- a mixture -- it is desirable in order to strengthen the film. 2000 or less % of the weight of a mixing ratio is desirable to a silicon compound. Further 10 - 1000 % of the weight is more desirable, and especially 20 - 500 % of the weight is desirable. Carbonaceous other metals can be used as an electric conduction agent. nickel, Cu, Ag, and Fe are desirable.

[0023] When the ratio of the lithium which can carry out insertion emission, and a silicon atom is expressed with Li_xSi as charge-and-discharge range of a silicon compound negative-electrode ingredient, $x=0-4.2$ are desirable. As a result of considering cycle-life amelioration of silicon wholeheartedly, when stopped in the range of $x=0-3.7$, the cycle life found out improving greatly. In $x=3.7$, it was about 0.05V to being [as opposed to / at charge potential / a lithium metal counter electrode] 0.0V in $x=4.2$ including an overvoltage. at this time, the configuration of a discharge curve changes and a flat discharge curve is obtained to the 0.5V (metal for a lithium) neighborhood by the 0.0V charge clinch -- receiving -- more than 0.05V -- especially -- more than 0.08V ($x=3.6$) -- about 0.4 -- the gently-sloping curve which has an average electrical potential difference in V is obtained. That is, having found out the phenomenon which the direction which raised the charge beginning-and-the-end electrical potential difference found out the specific phenomenon in which discharge potential fell, and the reversibility of a charge-and-discharge reaction also went up is shown.

[0024] Although the approach with the effectiveness of improving a cycle life had been described separately, maintaining the high capacity of a silicon compound, the still more desirable mode found out acquiring the still higher amelioration effectiveness with the combination of the above-mentioned approach.

[0025] In this invention, it is combinable with the compound which can carry out insertion emission of the lithiums, such as the other carbonaceous ingredient of the silicon compound of this invention, an oxide ingredient, a nitride ingredient, a sulfide ingredient, a lithium metal, and a lithium alloy, as a negative-electrode ingredient.

[0026] The positive-electrode ingredient used by this invention is a lithium content transition-metals oxide. It is the oxide which mainly contains at least one sort of transition-metals elements preferably chosen from Ti, V, Cr, Mn, Fe, Co, nickel, Mo, and W, and a lithium, and the mole ratio of a lithium and transition metals is the compound of 0.3 thru/or 2.2. It is the oxide which mainly contains more preferably at least one sort of transition-metals elements chosen from V, Cr, Mn, Fe, Co, and nickel, and a lithium, and the mole ratio of a lithium and transition metals is the compound of 0.3 thru/or 2.2. In addition, aluminum, Ga, In, germanium, Sn, Pb, Sb, Bi, Si, P, B, etc. may be contained in less than 30 mole percents to the transition metals which mainly exist. It is this better ** to use at least one sort of an ingredient which has a general formula Li_xMO_2 ($\text{M}=\text{Co}, \text{Fe}$ [nickel and Fe], Mn , $x=0-1.2$) or the Spinel

structure expressed with $\text{Li}_y\text{N}_x\text{Mn}_z\text{O}_4$ ($\text{N}=\text{Mn}$ $y=0-2$) in the above-mentioned positive active material. Specifically Li_xCoO_2 , Li_xNiO_2 , and Li_xMnO_2 , Li_xCo nickel1-a O_2 and Li_xCo V1-b O_2 , Li_xCo Fe1-b O_2 , Li_xMn O_4 , and Li_xMn Co_2 -c O_4 , They are Li_xMn nickel2-c O_4 , Li_xMn V2-c O_4 , and Li_xMn Fe2-c O_4 (it is $x=0.02-1.2$, $a=0.1$ to 0.9 , $b=0.8$ to 0.98 , $c=1.6-1.96$, and $z=2.01-2.3$ here). As most desirable lithium content transition-metals oxide, Li_xCoO_2 , Li_xNiO_2 , Li_xMnO_2 , Li_xCo nickel1-a O_2 , Li_xMn O_4 , and Li_xCo V1-b O_2 ($x=0.02-1.2$, $a=0.1$ to 0.9 , $b=0.9$ to 0.98 , $z=2.01-2.3$) are raised. In addition, the value of x is a value before charge-and-discharge initiation, and is fluctuated by charge and discharge.

[0027] Although the positive active material used by this invention is compoundable with the approach and solution reaction which mix a lithium compound and a transition-metals compound and are calcinated, especially its calcinating method is desirable. The detail for baking is indicated by the paragraph 35 of JP,6-60,867,A, JP,7-14,579,A, etc., and these approaches can be used for it. The positive active material obtained by baking may be used after water, aqueous acids, an alkaline water solution, and an organic solvent wash. Furthermore, you may be the approach of compounding by making it react to transition-metals oxide with a lithium metal, a lithium alloy, butyl lithium, and transition-metals oxide as an approach of inserting a lithium ion chemically.

[0028] Although especially the average grain size of the positive active material used by this invention is not limited, 0.1-50 micrometers is desirable. It is desirable that the volume of a 0.5-30-micrometer particle is 95% or more. It is still more desirable that the volume which a particle group with a particle size of 3 micrometers or less occupies is 18% or less of a whole product, and the volume which 15-micrometer or more particle group 25 micrometers or less occupies is 18% or less of a whole product. Although not limited especially as a specific surface area, 0.01-50 m^2/g is especially desirable at a BET adsorption method, and $\text{g-1m}^2/[\text{ of } 0.2\text{m}^2/\text{g}]$ is desirable. Moreover, as pH of the supernatant when melting 5g of positive active material to 100ml of distilled water, 12 or less [7 or more] are desirable.

[0029] When obtaining the positive active material of this invention by baking, it is 700-1200 degrees C that it is 500-1500 degrees C as a burning temperature desirable still more preferably, and it is 750-1000 degrees C especially preferably. As firing time, 4 - 30 hours is 6 - 20 hours desirable still more preferably, and it is 6 - 15 hours especially preferably.

[0030] If the electric conduction agent used for the mixture of this invention is an electronic conduction nature ingredient which does not cause a chemical change in the constituted cell, it is good anything. As an example, natural graphites, such as flaky graphite, a scale-like graphite, and an earthy graphite, petroleum coke, Elevated-temperature baking objects, such as coal corks, celluloses, a saccharide, and a mesophase pitch, Graphite, such as artificial graphites, such as a vapor growth graphite, acetylene black, Furnace black, KETCHIEN black, channel black, lamp black, Carbon black, such as thermal black, an asphalt pitch, a coal tar, Conductive metallic oxide, such as conductive whiskers, such as metal powders, such as conductive fiber, such as carbon materials, such as activated carbon, a meso fuze pitch, and the poly acene, and a metal fiber, copper, nickel, aluminum, and silver, a zinc oxide, and potassium titanate, and titanium oxide, etc. can be mentioned. It is desirable when an aspect ratio uses five or more plate-like things in a graphite. In these, graphite and carbon black are desirable, the magnitude of a particle has 0.01 micrometers or more and desirable 20 micrometers or less, and its particle (0.02 micrometers or more and 10 micrometers or less) is more desirable. These may be used independently and may use two or more sorts together. It is desirable when using together, and a 1-15-micrometer graphite particle is used together with carbon black, such as acetylene black. As for the addition to the binder layer of an electric conduction agent, it is desirable that it is 1 - 50 % of the weight to a negative-electrode ingredient or a positive-electrode ingredient, and it is especially desirable that it is 2 - 30 % of the weight. In carbon black or graphite, it is desirable that it is especially 3 - 20 % of the weight.

[0031] this invention -- an electrode -- a binder is used in order to hold a mixture. As an example of a binder, the polymer which has polysaccharide, thermoplastics, and rubber elasticity is mentioned. As a desirable binder, starch, a carboxymethyl cellulose, A cellulose, diacetyl cellulose, methyl cellulose, hydroxyethyl cellulose, Hydroxypropylcellulose, alginic-acid Na, polyacrylic acid, Polyacrylic acid Na, a polyvinyl phenol, polyvinyl methyl ether, Polyvinyl alcohol, a polyvinyl pyrrolidone, polyacrylamide,

Water-soluble polymers, such as PORIHIDOROKISHI (meta) acrylate and a styrene-maleic-acid copolymer, Polyvinyl chloride, poly tetrapod FURURO ethylene, polyvinylidene fluoride, A tetra-FURURO ethylene-hexa FURURO propylene copolymer, a vinylidene fluoride-tetra-FURURO ethylene-hexa FURURO propylene copolymer, Polyethylene, polypropylene, an ethylene-propylene-diene terpolymer (EPDM), Sulfonation EPDM, polyvinyl-acetal resin, a methylmetaacrylate, The acrylic ester (meta) copolymer containing acrylic ester (meta), such as 2-ethylhexyl acrylate, The polyvinyl ester copolymer containing vinyl ester, such as an acrylic ester-acrylonitrile copolymer and vinyl acetate, (Meta) A styrene-butadiene copolymer, an acrylonitrile-butadiene copolymer, Polybutadiene, neoprene rubber, a fluororubber, polyethylene oxide, An emulsion (latex) or suspension, such as polyester polyurethane resin, polyether polyurethane resin, polycarbonate polyurethane resin, polyester resin, phenol resin, and an epoxy resin, can be mentioned. The latex of a polyacrylic ester system, a carboxymethyl cellulose, polytetrafluoroethylene, and polyvinylidene fluoride are mentioned especially. It is desirable to use what distributed minute powder in water, as for these binders, it is more desirable to use that whose average size of the particle in dispersion liquid is 0.01-5 micrometers, and it is desirable especially to use what is 0.05-1 micrometer. these binders are independent -- or it can mix and use. if there are few additions of a binder -- an electrode -- the holding power and cohesive force of a mixture are weak. If many [too], the electrode volume will increase and electrode unit volume or the capacity per unit weight will decrease. The addition of a binder has 1 - 30 desirable % of the weight at such a reason, and 2 - 10 % of the weight is especially desirable.

[0032] In the constituted cell, a bulking agent can be used anything, if it is the fibrous ingredient which does not cause a chemical change. Usually, fiber, such as olefin system polymers, such as polypropylene and polyethylene, glass, and carbon, is used. Although especially the addition of a filler is not limited, 0 - 30 % of the weight is desirable. The object known as an inorganic and organic solid electrolyte can be used for an ion electric conduction agent, and it is indicated by the term of the electrolytic solution for details. A pressure enhancement agent is a compound which raises the internal pressure of a cell, and carbonates, such as a lithium carbonate, are the examples of representation.

[0033] Next, the configuration of the forward negative electrode in this invention is explained. the forward negative electrode -- both sides of a charge collector -- an electrode -- it is desirable that it is the gestalt which applied the mixture. In this case, even if the number of layers per one side is one layer, it may consist of more than two-layer. When the number of the layers per one side is two or more, a positive-active-material (or negative-electrode ingredient) content layer may be more than two-layer. A more desirable configuration is the case where it consists of a layer containing positive active material (or negative-electrode ingredient), and a layer which does not contain positive active material (or negative-electrode ingredient). There are an interlayer between the protective layer for protecting the layer containing positive active material (or negative-electrode ingredient) and the divided positive-active-material (or negative-electrode ingredient) content layer, an under coat between a positive-active-material (or negative-electrode ingredient) content layer and a charge collector, etc. in the layer which does not contain positive active material (or negative-electrode ingredient), and these are named generically in this invention and it is called an auxiliary layer.

[0034] As for a protective layer, it is desirable that it is in either both forward negative electrodes or the forward negative electrode. When inserting a lithium in a negative-electrode ingredient within a cell, as for a negative electrode, it is desirable that it is the gestalt which has a protective layer. A protective layer consists of at least one layer, and may be constituted by congener or two or more layers of a different kind. Moreover, you may be the gestalt which has a protective layer only on one side of the binder layers of both sides of a charge collector. These protective layers consist of particles, binders, etc. of water-insoluble nature. a binder -- the above-mentioned electrode -- the binder used in case a mixture is formed can be used. As a particle of water-insoluble nature, a various conductive particle and the organic and inorganic particle which does not have conductivity substantially can be used. The solubility to the water of a water-insoluble nature particle is 100PPM. The following and a desirable insoluble thing are desirable. The rate of the particle contained in a protective layer has 2.5 % of the weight or more and 96 desirable % of the weight or less, 5 % of the weight or more and its 95 % of the weight or

less are more desirable, and 10 % of the weight or more and especially its 93 % of the weight or less are desirable.

[0035] As a conductive particle of water-insoluble nature, carbon particles, such as a metal, a metallic oxide, a metal fiber, a carbon fiber, carbon black, and a graphite, can be mentioned. In these water-insoluble conductive particles, what has low reactivity with alkali metal, especially a lithium is desirable, and metal powder and a carbon particle are more desirable. As electrical resistivity in 20 degrees C of the element which constitutes a particle, it is 5×10^9 . Below $\omega\text{-m}$ is desirable.

[0036] As metal powder, a metal with low reactivity with a lithium, i.e., the metal which cannot make a lithium alloy easily, is desirable, and, specifically, copper, nickel, iron, chromium, molybdenum, titanium, a tungsten, and a tantalum are desirable. A needle, a column, tabular, and massive any are sufficient as the form of such metal powder, 0.02 micrometers or more and 20 micrometers or less have a desirable overall diameter, and it is more desirable. [of 0.1 micrometers or more and 10 micrometers or less] That [its] to which the front face has not oxidized too much is desirable, and when having oxidized, as for such metal powder, heat-treating by reducing atmosphere is desirable.

[0037] The well-known carbon material used as an electrical conducting material used together as a carbon particle when an electrode active material is not conductivity conventionally can be used. concrete -- an electrode -- the electric conduction agent used in case a mixture is made is used.

[0038] As a water-insoluble nature particle which does not have conductivity substantially, the impalpable powder of Teflon, SiC, alumimium nitride, an alumina, a zirconia, a magnesia, a mullite, forsterite, and a steatite can be mentioned. When these particles may be used together with a conductive particle and used by 0.01 or more times of a conductive particle, and 10 or less times, they are desirable.

[0039] A forward (negative) electrode sheet can be created by applying, drying and compressing the mixture of a forward (negative) pole on a charge collector. Positive active material (or negative-electrode ingredient) and an electric conduction agent are mixed, a binder (the suspension of resin fine particles or emulsion-like thing) and a dispersion medium are added, kneading mixing is carried out, succeedingly, it can distribute by stirring mixers, such as a mixer, a homogenizer, a dissolver, a planetary mixer, a paint shaker, and a sand mill, and the disperser, and preparation of a mixture can be performed. Water is desirable although water or an organic solvent is used as a dispersion medium. In addition, additives, such as a bulking agent, an ion electric conduction agent, and a pressure enhancement agent, may be added suitably. As for pH of dispersion liquid, in a negative electrode, 7-12 are desirable at 5-10, and a positive electrode.

[0040] Although spreading can be performed by various approaches, the reverse roll method, the direct rolling method, the blade method, the knife method, the extrusion method, a slide agglutination test, the curtain method, the gravure method, the bar method, a dip method, and the squeeze method can be mentioned, for example. The approach using an extrusion die and especially the approach using a slide coating machine are desirable. As for spreading, it is desirable to carry out the rate for 0.1-100m/. under the present circumstances, a mixture -- according to the liquid nature of a paste, and drying, the surface state of a good spreading layer can be acquired by selecting the above-mentioned method of application. It is desirable from viewpoints, such as manufacture of a uniform electrode, and a manufacturing cost, to apply two or more of those layers to coincidence, when electrode layers are two or more layers. The thickness, die length, and width of the spreading layer are decided with the magnitude of a cell. The thickness of a typical spreading layer is 10-1000 micrometers in the condition of having been compressed after desiccation. The electrode sheet after spreading is dried and dehydrated by hot blast, a vacuum, infrared radiation, far infrared rays, an electron ray, and the operation of the damp style. these approaches are independent -- or it can combine and use. The range of drying temperature of 80-350 degrees C is desirable, and its range which is 100-260 degrees C is especially desirable. The moisture content after desiccation has desirable 2000 ppm or less, and its 500 ppm or less are more desirable. Although compression of an electrode sheet can use the press approach generally adopted, a die-press method and its calender pressing method are especially desirable. Especially press ** is 10kg/cm² - 3 t/cm², although not limited. It is desirable. The pressing speed of the calender pressing method has the amount of desirable 0.1-50m/. Press temperature has desirable room temperature -200 degree C.

[0041] The separator which can be used by this invention has large ion transmittance, and it has a predetermined mechanical strength, and that what is necessary is just an insulating thin film, as the quality of the material, an olefin system polymer, a fluorine system polymer, a cellulose system polymer, polyimide, nylon, a glass fiber, and an alumina fiber are used, and a nonwoven fabric, textile fabrics, and a microporous film are used as a gestalt. Especially, as the quality of the material, the mixture of polypropylene, polyethylene, polypropylene, the mixture of polyethylene and polypropylene, and Teflon and the mixture of polyethylene and Teflon are desirable, and what is a microporous film as a gestalt is desirable. Especially, the microporous film whose aperture is 0.01-1 micrometer and whose thickness is 5-50 micrometers is desirable. Even if these microporous films are independent film, they may be complex films which consist of more than two-layer [from which properties, such as a configuration, a consistency, etc. of a fine hole, and the quality of the material, differ]. For example, the complex film which made the polyethylene film and the polypropylene film rival can be mentioned.

[0042] Generally the electrolytic solution consists of a supporting electrolyte and a solvent. As for the supporting electrolyte in a lithium secondary battery, lithium salt is mainly used. As lithium salt which can be used by this invention, for example LiClO_4 , LiBF_4 , LiPF_6 , LiCF_3CO_2 , and LiAsF_6 , LiSbF_6 , $\text{LiB}_{10}\text{Cl}_{10}$, the fluorosulfonic acid expressed with $\text{LiOSO}_2\text{C}_n\text{F}_{2n+1}$ (n is six or less positive integer), the imide salt (m --) expressed with $\text{LiN}(\text{SO}_2\text{C}_n\text{F}_{2n+1})(\text{SO}_2\text{C}_m\text{F}_{2m+1})$ the methide salt (p --) as which n is expressed in six or less positive integer and $\text{LiC}(\text{SO}_2\text{C}_p\text{F}_{2p+1})(\text{SO}_2\text{C}_q\text{F}_{2q+1})(\text{SO}_2\text{C}_r\text{F}_{2r+1})$, respectively q and r , respectively Six or less positive integer, a low-grade aliphatic-carboxylic-acid lithium, Li salts, such as LiAlCl_4 , LiCl , LiBr , LiI , a chloro borane lithium, and 4 phenyl lithium borate, can be raised, and these kinds or two sorts or more can be mixed and used. It is LiBF_4 especially. And/or LiPF_6 What was dissolved is desirable. Although especially the concentration of a supporting electrolyte is not limited, its 0.2-3 mols per 1l. of electrolytic solutions are desirable.

[0043] As a solvent which can be used by this invention, propylene carbonate, ethylene carbonate, Butylene carbonate, chloroethylene carbonate, carbonic acid trifluoro methyl ethylene, Carbonic acid difluoro methyl ethylene, carbonic acid mono-fluoro methyl ethylene, 6 methyl-fluoride acetate, 3 methyl-fluoride acetate, dimethyl carbonate, Diethyl carbonate, methylethyl carbonate, gamma-butyrolactone, Methyl formate, methyl acetate, 1, 2-dimethoxyethane, a tetrahydrofuran, 2-methyl tetrahydrofuran, dimethyl sulfoxide, 1, 3-dioxolane, The 2 and 2-screw (trifluoromethyl) -1, 3-dioxolane, a formamide, Dimethylformamide, dioxolane, dioxane, an acetonitrile, Nitromethane, ethyl mono-glyme, trialkyl phosphate, boric-acid triester, Trimethoxy methane, a dioxolane derivative, a sulfolane, 3-methyl-2-oxazolidinone, 3-alkyl sydnone (an alkyl group is propyl, isopropyl, butyl, etc.), Aprotic organic solvents, such as propylene carbonate derivative, tetrahydrofuran derivative, ethyl ether, 1, and 3-propane ape ton, can be mentioned, and these kinds or two sorts or more are mixed and used. In these, the solvent of a carbonate system is desirable and it is desirable especially to mix and use annular carbonate and un-annular carbonate. As annular carbonate, ethylene carbonate and propylene carbonate are desirable. moreover -- as un-annular carbonate -- diethyl carbonate, dimethyl carbonate, and methylethyl carbonate -- ** -- it is desirable. As the electrolytic solution which can be used by this invention, they are LiCF_3SO_3 , LiClO_4 , and LiBF_4 to the electrolytic solution which mixed suitably ethylene carbonate, propylene carbonate, 1, 2-dimethoxyethane, dimethyl carbonate, or diethyl carbonate. And/or, LiPF_6 The included electrolytic solution is desirable. To one [at least] mixed solvent of propylene carbonate, at least one side of ethylene carbonate and dimethyl carbonate, or diethyl carbonate, they are LiCF_3SO_3 , LiClO_4 , or LiBF_4 especially. At least a kind of salt and LiPF_6 which were chosen from inside The included electrolytic solution is desirable. Especially the amount that adds these electrolytic solutions in a cell is not limited, but can be used according to the amount of a positive-electrode ingredient or a negative-electrode ingredient, or the size of a cell.

[0044] Moreover, the following solid electrolytes can also be used together besides the electrolytic solution. It is divided into an inorganic solid electrolyte and an organic solid electrolyte as a solid electrolyte. The nitride of Li, the halogenide, the oxygen acid salt, etc. are well known by the inorganic solid electrolyte. Especially, Li_3N , LiI , Li_5NI_2 , $\text{Li}_3\text{N-LiI-LiOH}$, Li_4SiO_4 , $\text{Li}_4\text{SiO}_4\text{-LiI-LiOH}$, $x\text{Li}_3\text{PO}_4\text{-(1-x)Li}_4\text{SiO}_4$, Li_2SiS_3 , a phosphorus sulfide compound, etc. are effective.

[0045] The macromolecule matrix material which made the polymer which contains the polymer, the polypropylene oxide derivative, or this derivative containing a polyethylene oxide derivative or this derivative in an organic solid electrolyte, the polymer containing an ionic dissociation radical, the polymer containing an ionic dissociation radical, the mixture of the above-mentioned aprotic electrolytic solution and a phosphoric ester polymer, and the aprotic polar solvent contain is effective. Furthermore, there is also the approach of adding a polyacrylonitrile to the electrolytic solution. Moreover, how to use inorganic and an organic solid electrolyte together is also learned.

[0046] Moreover, other compounds may be added to an electrolyte in order to improve discharge and a charge-and-discharge property. For example, a pyridine, pyrroline, a pyrrole, a triphenylamine, a phenyl carbazole, A triethyl FOSU fight, triethanolamine, cyclic ether, Ethylenediamine, n-glyme, hexalin acid TORIAMIDO, a nitrobenzene derivative, Sulfur, a quinonimine dye, N-permutation oxazolidinone, and N and N'-permutation imidalidinone, Ethylene glycol dialkyl ether, quaternary ammonium salt, a polyethylene glycol, A pyrrole, 2-methoxyethanol, $AlCl_3$, the monomer of a conductive polymer electrode active material, The triethylenephosphoramidate, trialkylphosphine, a morpholine, The crown ether like an aryl compound with a carbonyl group and 12-crown -4, hexamethylphosphoric triamide and 4-alkyl morpholine, the bicyclic third class amine, oil, the fourth class phosphonium salt, the third class sulfonium salt, etc. can be mentioned. Especially a desirable thing is independent or the case where it combined and uses, about a triphenylamine and a phenyl carbazole.

[0047] Moreover, in order to make the electrolytic solution into incombustibility, a halogen-containing solvent, for example, a carbon tetrachloride, and a 3 fluoridation ethylene chloride can be included in the electrolytic solution. Moreover, in order to give fitness to elevated-temperature preservation, carbon dioxide gas can be included in the electrolytic solution.

[0048] As for the electrolytic solution, it is desirable not to contain a part for moisture and a free acid as much as possible. For this reason, as for the raw material of the electrolytic solution, what carried out sufficient dehydration and purification is desirable. Moreover, the inside of the dry air not more than minus 30 degree C or inert gas has [adjustment of the electrolytic solution] a desirable dew-point. 0.1-500 ppm of amounts for the moisture in the electrolytic solution and a free acid are 0.2-100 ppm more preferably.

[0049] Although the electrolytic solution may pour in the whole quantity at once, it is desirable to pour in in 2 steps or more. When pouring in in 2 steps or more, the presentation (after pouring in the solution which dissolved lithium salt in the non-aqueous solvent or the non-aqueous solvent, the solution which dissolved lithium salt in a non-aqueous solvent or a non-aqueous solvent with viscosity higher than said solvent is poured in) which is different also by the same presentation is sufficient as each liquid. Moreover, a cell can may be decompressed for compaction of the impregnation time amount of the electrolytic solution etc., or you may perform applying a centrifugal force and a supersonic wave to a cell can.

[0050] The cell cans and cell lids which can be used by this invention are the iron steel plate which performed nickel plating as the quality of the material, a stainless steel plate (SUS304, SUS304 L, SUS304 N, SUS316, SUS316 L, SUS430, SUS444 grade), the stainless steel plate (same as the above) which performed nickel plating, aluminum or its alloy, nickel, titanium, and copper, and are perfect circle form tubed, ellipse form tubed, square tubed, and rectangle tubed as a configuration. Especially when a sheathing can serves as a negative-electrode terminal, a stainless steel plate and the iron steel plate which performed nickel plating are desirable, and when a sheathing can serves as a positive-electrode terminal, a stainless steel plate, aluminum, or its alloy is desirable. Any, such as a carbon button, coin, a sheet, a cylinder, and an angle, are sufficient as the configuration of a cell can. A relief valve can be used for an obturation plate as a cure of an internal pressure rise of a cell can. In addition, the approach of putting in slitting can also be used for members, such as a cell can and a gasket. In addition, it may be equipped with the various insurance components (a fuse, bimetal, a PTC component, etc. as [For example,] an overcurrent-protection component) known from the former.

[0051] Metals (for example, iron, nickel, titanium, chromium, molybdenum, copper, aluminum, etc.) with electrical conductivity and those alloys can be used for the lead plate used by this invention. A

well-known approach (electric welding of an example, a direct current, or an alternating current, laser welding, ultrasonic welding) can be used for the welding process of a cell lid, a cell can, an electrode sheet, and a lead plate. The compound and mixture which are known from the former, such as asphalt, can be used for the sealing compound for obturation.

[0052] As the quality of the material, they are an olefin system polymer, a fluorine system polymer, a cellulose system polymer, polyimide, and a polyamide, from organic solvent-proof nature and low-water-flow part permeability, the gasket which can be used by this invention has a desirable olefin system polymer, and especially its polymer of a propylene subject is desirable. Furthermore, it is desirable that it is the block copolymerization polymer of a propylene and ethylene.

[0053] As for the cell assembled as mentioned above, it is desirable to perform aging processing. There are pretreatment, activation, after treatment, etc. in aging processing, and the cell which was excellent in a high charge-and-discharge capacity and cycle nature by this can be manufactured. Pretreatment is processing for equalizing distribution of the lithium in an electrode, for example, combination of the arbitration of the temperature control for making dissolution control of a lithium and distribution of a lithium into homogeneity, rocking and/or rotation processing, and charge and discharge is performed. Activation is processing for making a lithium insert to the negative electrode of a cell proper, and it is desirable to insert 50 - 120% of the amount of lithium insertion at the time of real use charge of a cell. After treatment is processing for fully carrying out activation, has this [the preservation processing for making a cell reaction into homogeneity, and / for a judgment / charge-and-discharge processing], and can be combined with arbitration.

[0054] The desirable aging conditions before activation of this invention (pretreatment conditions) are as follows. 30 degrees C or more 70 degrees C or less of temperature are desirable, it is more desirable, and is still more desirable. [of 40 degrees C or more 60 degrees C or less] [of 30 degrees C or more 60 degrees C or less] Moreover, as for open circuit voltage, less than [more than 2.5V3.8V] is desirable, less than [more than 2.5V3.5V] is more desirable, and less than [more than 2.8V3.3V] is still more desirable. An aging period will have 20 or less desirable days the 1st day or more, and will be desirable the 1st day or more. [of especially 15 or less days] As for the charge electrical potential difference of activation, more than 4.0V is desirable, less than [more than 4.05V4.3V] is more desirable, and less than [more than 4.1V4.2V] is still more desirable. As aging conditions after activation, less than [more than 3.9V4.3V] has desirable open circuit voltage, especially less than [more than 4.0V4.2V] is desirable, 30 degrees C or more 70 degrees C or less of temperature are desirable, and it is desirable. [of 40 degrees C or more especially 60 degrees C or less] An aging period will have 20 or less desirable days the 0.2nd day or more, and will be desirable the 0.5th day or more. [of especially five or less days]

[0055] The cell of this invention is covered with a sheathing material if needed. As a sheathing material, there are heat-shrinkable tubing, adhesive tape, a metal film, paper, cloth, a coating, a plastics case, etc. Moreover, the part of sheathing discolored with heat in part at least is prepared, and you may make it the heat history in use known.

[0056] The cell of this invention constructs two or more to a serial and/or juxtaposition if needed, and is contained by the cell pack. A safety circuit (circuit with the function which intercepts a current if it acts as the monitor of the electrical potential difference of each cell and/or the whole group cell, temperature, the current, etc. and is required) besides insurance components, such as a forward temperature coefficient resistor, a thermal fuse, a fuse, and/or a current cutoff component, may be prepared in a cell pack. Moreover, the positive electrode of each cell and a negative-electrode terminal, the whole group cell and the temperature detection terminal of each cell, the current detection terminal of the whole group cell, etc. can also be prepared in a cell pack as an external terminal in addition to the positive electrode of the whole group cell, and a negative-electrode terminal. Moreover, electrical-potential-difference conversion circuits (DC-DC converter etc.) may be built in a cell pack. Moreover, you may fix by welding a lead plate, and connection of each cell may be fixed so that it can detach and attach easily with a socket etc. Furthermore, display functions, such as cell remaining capacity, existence of charge, and a use count, may be prepared in a cell pack.

[0057] The cell of this invention is used for various devices. It is desirable to be especially used for a video movie, a pocket mold videocassette recorder with a built-in monitor, a movie camera with a built-in monitor, a digital camera, a compact camera, a single-lens reflex camera, a disposable camera, a notebook sized personal computer, a note type word processor, an electronic notebook, a cellular phone, a cordless telephone, a mustached camber, a power tool, an electric mixer, an automobile, etc.

[0058]

[Example] Although an example is raised to below and this invention is explained in more detail, unless the main point of invention is exceeded, this invention is not limited to an example.

[0059] As an example 1 negative-electrode ingredient, as a polycrystal silicon simple substance (compound -1) and an alloy compound of the following compounded metallurgically A Si-Ag alloy (compound-2 weight ratio 40-60), the silicon which ground the silicon to which elution of the Li was carried out using isopropyl alcohol in argon gas, and was obtained from Li₄ Si compounded metallurgically (compound -3), Si-SiO₂ (compound-4 weight ratio 90-10) which made fine particles the solid which mixed colloidal silica with polycrystal silicon, and was heated and obtained at 1000 degrees C in the vibration mill in argon gas, Si which carried out Ag plating as a compound galvanized on the polycrystal silicon front face by the nonelectrolytic plating method (weight ratio of compound-5 Si-Ag 40-60), 30g of silicon was added in the liquid which melted 3g of polyvinylidene fluorides to N-methyl pyrrolidone 50g, after carrying out mixed kneading, it dried and the fine particles (compound -6) ground with the automatic mortar were used. Each average grain size of the above-mentioned negative-electrode ingredient (compounds 1-6) used the particle of the range of 0.05-4 micrometers. Next, 10g of polyvinylidene fluorides was distributed for the fine particles which fully mixed the scale-like natural graphite of same weight with silicon, and were obtained to 500ml of N-methyl-2-pyrrolidones as 190g and a binder, and the negative-electrode paste was created.

[0060] positive-active-material LiCoO₂ 200g and acetylene black 10g -- a homogenizer -- mixing -- continuing -- as a binder -- 5g of polyvinylidene fluorides -- mixing -- 500ml of N-methyl-2-pyrrolidones -- adding -- kneading mixing -- carrying out -- a positive electrode -- a mixture -- the paste was created.

[0061] the positive electrode created above -- a mixture -- compression molding of the paste was carried out with the roller press machine after spreading and 150-degree-C desiccation to both sides of an aluminium foil charge collector with a thickness of 30 micrometers by the blade coating machine, it judged in predetermined magnitude, and the band-like positive-electrode sheet was created. Furthermore, dehydration desiccation was enough carried out at the far-infrared heater all over the dry box (dew-point; dry air -50 degrees C or less), and the positive-electrode sheet was created. the same -- a negative electrode -- a mixture -- the paste was applied to the metallic foil charge collector (copper, nickel, titanium, stainless steel) of 0.07 micrometers of 20-micrometer surface roughness, and the negative-electrode sheet was created by the same approach as the above-mentioned positive-electrode sheet creation. the charge capacity of coverage of a forward negative electrode of the 1st cycle from which the charge capacity of the 1st cycle from which positive active material is set to 4.2V to a lithium metal, and the above-mentioned negative-electrode ingredient are set to 0.0V suits -- as -- each electrode -- the coverage of a mixture was adjusted.

[0062] Next, the electrolytic solution was created as follows. In the argon ambient atmosphere, 65.3g diethyl carbonate was put into the polypropylene container of 200 cc thin opening, and 22.2g ethylene carbonate was dissolved small quantity every, taking care that solution temperature does not exceed 30 degrees C to this. Next, 0.4g LiBF₄ and 12.1g LiPF₆ It dissolved in the above-mentioned polypropylene container small quantity every in order, respectively, taking care that solution temperature does not exceed 30 degrees C. The obtained electrolytic solution was a transparent and colorless liquid by specific gravity 1.135. The amount of [18 ppm (product made from the Kyoto electron it measures with trade name MKC-210 mold Carl Phi Shah water measurement equipment) and] free acid of moisture was 24 ppm (the bromthymol blue is used as an indicator, a neutralization titration is carried out using a decinormal NaOH water solution, and it measures).

[0063] The cylinder cell was created as follows. How to make a cell according to drawing 1 is

explained. The laminating of the separator was carried out to the positive-electrode sheet created above, the separator made from a microporous polyethylene film, and the negative-electrode sheet pan at order, and this was wound around the curled form. It contained with the iron closed-end cylindrical cell can (1) which performed nickel plating which serves this wound electrode group (2) as a negative-electrode terminal, and the up electric insulating plate (3) was inserted further. what carried out the laminating of a positive-electrode terminal (6), an insulating ring, a PTC component (63), a current cutoff object (62), and the pressure induction valve element (61) after pouring in the above-mentioned electrolytic solution into this cell can -- a gasket (5) -- minding -- the cylindrical cell was created in total.

[0064] The above-mentioned cylindrical shape cell is charged by 1.5A. In this case, it charged by constant current to 4.2V, and charge controlled the charging current to keep it constant by 4.2V until 2.5 hours had passed since charge initiation. Discharge was carried out according to constant current to 3.0V with the 0.2C current. the discharge capacity of the 1st cycle at that time, average discharge voltage, and the amount of energy (discharge capacity x average discharge voltage) -- the capacity maintenance factor of 30 cycle eye which repeated charge and discharge was shown in Table 1 again.

[0065]

Table 1 cell Negative electrode Negative-electrode charge collector Discharge capacity Average discharge The amount of energy Cycle-life number Ingredient Quality of the material (mAh) Electrical potential difference (V) (Wh) (30 cycle %) ----- 1 1 Cu 2100 3.5 7.4 80 2 1 nickel 2200 3.5 7.7 83 3 1 Ti 2000 3.5 7.0 80 4 1 SUS304 2200 3.5 7.7 82 5 2 Cu 2100 3.5 7.4 82 6 2 nickel 20003. 5 7.085 7 2 Ti 2100 3.5 7.3 78 8 2 SUS304 2000 3.5 7.0 819 3 Cu 2200 3.57.7 8210 3nickel 2100 3.5 7.4 8611 3Ti2100 3.5 7.3 7012 3 SUS304 2000 3.5 7.0 7813 4 Cu 21003. 5 7.48214 4 nickel 2200 3.5 7.7 8215 4 Ti 2100 3.5 7.4 8116 4 SUS304 20003.5 7.07817 5 Cu 2000 3.5 7.0 7518 5 nickel 2100 3.5 7.4 80195 Ti2000 3.5 7.0 7820 5 SUS304 2100 3.5 7.4 81216 Cu 2000 3.57.0 7822 6 nickel 2000 3.5 7.0 75236 Ti 2100 3.5 7.4 8124 6SUS304 2200 3.57.7 82 [0066] The cells 25-28 as well as a cell 1 were produced except setting surface roughness of the copper foil of the negative-electrode charge collector of the cell 1 of example -2 example -1 to 0.03 micrometers, 0.05 micrometers, 0.1 micrometers, and 1 micrometer. Next, the cell for a comparison was made as follows. The comparison cell 30 as well as [completely] a cell 1 was made except changing [the comparison cell 29] the negative-electrode charge collector of a cell 1 into the aluminium foil whose surface roughness is 0.1 micrometers in 20 micrometers in thickness for the negative-electrode charge collector of a cell 1 completely like a cell 1 except changing into the copper foil whose surface roughness is 0.01 micrometers by 20 micrometers in thickness. Using these cells 25-30, the same trial as an example 1 was performed, and the result of Table 2 was obtained.

[0067]

Table 2 cell Negative electrode Collection of negative electrodes Negative-electrode charge collector ***** Discharge energy Cycle-life number Ingredient ***** Surface roughness mum Amount mAh *****V RUGI Wh 30 cycle % 25 1 Copper 0.03 2060 3.5 7.2 7026 1 Copper 0.05 2100 3.5 7.4 7827 1 Copper 0.1 2100 3.5 7.4 8028 1 Copper 1.0 2080 3.5 7.3 7529 1 Copper 0.01 2030 3.57.1 60301 Aluminum 0.1 2200 3.57.7 49 [0068] Although the negative-electrode sheet for a comparison as well as the negative electrode of a cell 1 was created except using the copper foil whose thickness is 20 micrometers and whose surface roughness is furthermore 2 micrometers about the negative-electrode charge collector of a cell 1 and production of a cell 31 was tried, it turned out that this negative-electrode sheet causes cutting failure in a spreading process, and there is no process stability.

[0069] A comparison of the cells 1-28 and the comparison cell 30 using a charge collector of this invention improves the cycle life for the direction which used copper, titanium, nickel, and a stainless foil compared with the case where aluminium foil is used. Furthermore, surface roughness was understood that 0.03 micrometers or more and 1 micrometer or less are suitable from the comparison of cells 25-28 and cells 29 and 31. Moreover, positive active material LiCoO₂ used in the example LiNiO₂ LiMn 2O₄ Even if changed, the same effectiveness as examples 1 and 2 was acquired.

[0070]

[Effect of the Invention] According to this invention, the nonaqueous rechargeable battery the amount of

energy and whose cycle life improved can be obtained.

[Translation done.]